DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 37

IODINE NUMBER OF LINSEED AND PETROLEUM OILS

BY

W. H. SMITH, Assistant Chemist

and

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Bureau of Standards

[APRIL 28, 1914]

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CONTENTS

I. INTRODUCTION

The linseed oil used in the manufacture of printing ink is of the so-called "burnt" type. There are two general processes for its manufacture—one in which the oil is heated until the vapors take fire and continue to burn, the oil being allowed to burn until it attains the desired viscosity; and a second in which the oil is heated without permitting it to take fire.

Burnt oil is prepared in several grades, all differing from the raw oil in an increase of viscosity, specific gravity, and acid number, and a decrease in the iodine number. The longer the oil is heated the greater these differences become.

In the determination of the iodine value of some burnt linseed oils difficulty was experienced in obtaining concordant results. Leeds [1] has published some figures for iodine absorption of lithographic oils. Kitt [2] has also published a series of results which show decrease in iodine absorption with increasing viscosity, but the figures do not agree with those given by Leeds. These determinations were made according to the Hübl method.[3] In recent years this method has been so generally replaced by the rapid and more

[1] J. Soc. Chem. Ind., 13, p. 203; 1894.
[2] Chem. Rev. Fett. u. Harz Ind., 8, p. 40, 1901; J. Soc. Chem. Ind., 20, p. 40, 1901.
[3] Dingler's Poly. J., 253, p. 281; J. Soc. Chem. Ind., 3, p. 641, 1884.

convenient Hanus [4] method that it was considered desirable to learn the values afforded by this method. Preliminary work developed the fact that small variations in the method employed produced varying results. It has been well established that iodine absorption includes not only the halogen taken up by unsaturated compounds, but that the substitution of halogen for hydrogen with the formation of halogen acid occurs simultaneously. Various methods for determining the amount of substitution have been suggested, with the view of obtaining a corrected value which would represent the addition only, but very little use has been made of them. It has been generally recognized that an excess of iodine is necessary, and it has been assumed that all oils are alike in the amount of excess required. The appended results obtained by us show that this is far from being true. Various quantities of iodine have been suggested as to the proper excess which should be present, but practically all of these are given in connection with discussions of the Hübl method, and may not hold true for the Hanus method. Furthermore, there has been a lack of uniformity in the use of the term "excess of iodine." In the tables which follow whenever this expression is used it shall be understood to mean that percentage of the total amount added which remains unchanged at the expiration of the time allowed for absorption.

II. PROCEDURE

The method employed was essentially the modification of the Hanus method suggested by Hunt.[5] Thirteen and two-tenths grams of iodine were dissolved in 1 liter of glacial acetic acid (99.9 per cent), and 3 cc of bromine added. This solution was always allowed to stand for some days before being used. The thiosulphate solution employed was approximately tenth normal, and was standardized by means of potassium bichromate. Standardization was repeated at frequent intervals. A freshly prepared starch solution was used; also a 10 per cent solution of potassium iodide, prepared in small amounts and kept in a brown bottle. The temperature of the room was maintained at 25° C

[4] Zs. Untersuch. Nahr. Genuss., 20, p. 913, 1901; J. Soc. Chem. Ind., 20, p. 1246, 1901.
[5] J. Soc. Chem. Ind., 21, p. 454; 1902.

to prevent variations caused by change of temperature. The reagents were of standard quality and errors caused by impurities were eliminated by running blanks with each series of determinations. When it was desired to use like amounts of an oil in a series of tests, 4 grams of the oil were dissolved in chloroform in a 200-cc graduated flask and the solution allowed to reach room temperature. Ten-cc portions of this solution, representing 0.2 gram of oil, were measured from a burette. The general procedure was as follows: The exact weight of oil was transferred to 250 to 300-cc glass-stoppered Jena bottles; the required amount of Hanus solution was added from a burette. The mixture was allowed to stand for exactly 30 minutes in a dark closet; 25 cc of the 10 per cent potassium iodide solution and 100 cc of water [6] were added,[7] and the excess of iodine was immediately titrated with thiosulphate.

The factors known to influence the iodine number are the temperature, the time of absorption, the weight of oil taken, and the excess of iodine present obtained by increasing the amount of iodine solution. The exact effect of each factor was studied by varying one at a time, this procedure being followed with a series of oils.

III. SAMPLES

The samples employed were as follows:

(*a*) A raw linseed oil, sample No. 3, of the four linseed oils tested by the American Society for Testing Materials [8] in 1909. This sample had been hermetically sealed, immediately upon completion of the tests in 1909, and had been kept in a cool dark closet.

(*b*) A boiled oil of the so-called "bunghole" variety.

(*c*) Four burnt linseed oils, Nos. 00, 1, 3, and 5. These oils were obtained from northwestern seed and, after refining, were heated in copper kettles at a temperature of 560 to 600° F until the desired consistency was attained.

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[6] Tolman and Munson: J. Am. Chem. Soc., 25, p. 244; 1903.

[7] Gill: "Oil Analysis," 6th ed., p. 62, footnote.

[8] See report of Committee E on Preservative Coatings for Structural Materials, Proceedings of the A. S. T. M., Vol. IX, p. 184; 1909, analyses by J. B. Tuttle. Another sample of this same oil was also tested in 1911, results of which are given in report of Subcommittee E of Committee D-1, Proceedings of the A. S. T. M., Vol. XI, pp. 23-30; 1911.

(*d*) Three petroleum oils. Two of these, marked light oil No. 1 and No. 2, were automobile cylinder oils, and the third was an engine oil. Upon analysis these oils gave the following figures:

	B. S. eng.	Light No. 1	Light No. 2
Flash	175°	220°	230°
Fire	210	265	280
Sp. gr. 20°/4°	0.9260	0.8738	0.9265
Carbonization (3 hrs. at 250°)	1.01%	0.11%	0.23%
Oxygen absorp. 144½ hours	1.60%	1.91%	1.90%
Original acidity (mg KOH, per g)	0.70	0.08	0.17
Acidity after exposure	13.52	14.39	13.83
Increase in acidity	12.82	14.31	13.66

The other constants of the samples were not determined, as they have no bearing on the present problem.

IV. RESULTS OF TESTS

TABLE 1

Linseed Oil

[Temperature, 25°; Time, 30 Minutes; 25-cc Hanus Solution; Weight of Oil Varied]

Oil	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Oil	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(a) Raw Oil					(a) Raw Oil—Continued				
0.0522	0.6669	0.0962	184.3	.....	0.6054	0.6669	0.6091	100.6	100.6
0.0522	0.6669	0.0970	185.8	.....	0.8013	0.6669	0.6191	77.3	77.3
0.0522	0.6669	0.0967	185.3	185.1	(b) Boiled Oil				
0.1044	0.6669	0.1940	185.8	.....	0.0600	0.6902	0.1066	177.6	.....
0.1044	0.6669	0.1955	187.3	.....	0.1181	0.6902	0.2102	178.0	.....
0.1044	0.6669	0.1949	186.7	186.6	0.1322	0.6902	0.2355	178.3	.....
0.1566	0.6669	0.2912	186.0	.....	0.1673	0.6902	0.2984	178.3	.....
0.1566	0.6669	0.2906	185.6	.....	0.2061	0.6902	0.3682	178.5	.....
0.1514	0.6669	0.2844	187.8	186.5	0.2220	0.6902	0.3962	178.4	.....
0.2004	0.6669	0.3735	186.4	.....	0.2523	0.6902	0.4438	175.7	.....
0.2004	0.6669	0.3746	186.4	186.4	0.2783	0.6902	0.4832	173.7	.....
0.2504	0.6669	0.4543	181.5	.....	0.2920	0.6902	0.4976	170.4	.....
0.2504	0.6669	0.4572	182.6	182.1	0.3217	0.6902	0.5250	163.2	.....
0.3027	0.6669	0.5098	168.4	.....	0.3328	0.6902	0.5346	160.6	.....
0.3027	0.6669	0.5098	168.4	168.4	0.3583	0.6902	0.5518	154.0	.....
0.4542	0.6669	0.5869	129.2	.....	0.3874	0.6902	0.5744	148.2	.....
0.4542	0.6669	0.5888	129.6	129.4	0.3969	0.6902	0.5848	147.4	.....
0.5008	0.6669	0.6071	121.2	.....	0.5550	0.6902	0.6344	114.0	.....
0.5008	0.6669	0.6103	121.9	121.5					

TABLE 1—Continued

Oil	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(c) Burnt Linseed Oil No. "00."				
0.1235	0.6811	0.1827	148.0	.....
0.1268	0.6811	0.1882	148.4	148.2
0.1465	0.6811	0.2154	147.0	147.0
0.1842	0.6811	0.2616	142.0	.....
0.1863	0.6811	0.2632	141.3	141.7
0.2539	0.6779	0.3401	133.0	.....
0.2506	0.6779	0.3297	131.6	132.3
0.3489	0.6779	0.4128	118.3	.....
0.3562	0.6779	0.4171	117.1	117.7
0.4490	0.6779	0.4658	103.7	.....
0.4497	0.6779	0.4658	103.6	103.6
0.6058	0.6779	0.5216	86.1	86.1
0.7831	0.6779	0.5583	71.3	71.3
(d) Burnt Linseed Oil No. 1				
0.0880	0.6787	0.1220	138.6	138.6
0.1891	0.6787	0.2480	131.1	.....
0.1917	0.6787	0.2512	131.0	131.0
0.2856	0.6787	0.3310	115.9	115.9
0.3577	0.6787	0.3788	105.9	.....
0.3595	0.6787	0.3796	105.6	105.8
0.4377	0.6787	0.4195	95.8	95.8
0.5853	0.6787	0.4753	81.2	81.2
(e) Burnt Linseed Oil No. 3				
0.1085	0.5846	0.1412	130.1	.....
0.1085	0.5846	0.1406	129.6	129.9
0.1632	0.5846	0.1962	120.2	.....
0.1632	0.5846	0.1948	119.4	119.8
0.2376	0.5846	0.2463	103.7	.....
(e) Burnt Linseed Oil No. 3—Contd				
0.2376	0.5846	0.2463	103.7	103.7
0.3264	0.5846	0.2937	90.0	.....
0.3264	0.5846	0.2944	90.2	90.1
0.4158	0.5846	0.3313	79.7	79.7
0.5346	0.5846	0.3612	67.6	67.6
0.6534	0.5846	0.3883	59.4	59.4
(f) Burnt Linseed Oil No. 5				
0.0517	0.5874	0.0671	130.0	.....
0.0517	0.5874	0.0668	129.2	.....
0.0517	0.5874	0.0682	131.9	130.4
0.1034	0.5874	0.1336	129.2	.....
0.1034	0.5874	0.1329	128.5	.....
0.1034	0.5874	0.1325	128.1	128.6
0.1551	0.5874	0.1858	119.8	.....
0.1551	0.5874	0.1858	119.8	119.8
0.2054	0.5860	0.2213	107.7	.....
0.2054	0.5860	0.2234	108.8	108.3
0.2423	0.5870	0.2468	101.9	.....
0.2423	0.5870	0.2464	101.7	101.8
0.2826	0.5870	0.2671	94.5	.....
0.2826	0.5870	0.2680	94.8	94.6
0.3634	0.5870	0.3016	83.0	83.0
0.4108	0.5860	0.3163	77.2	.....
0.4108	0.5860	0.3187	77.6	77.4
0.5249	0.5870	0.2883	66.8	66.8
0.6162	0.5860	0.3711	60.2	.....
0.6162	0.5860	0.3688	59.9	60.0
0.7268	0.5870	0.3810	52.4	52.4

TABLE 2

Linseed Oil

[Temperature, 25°; 0.2-g Oil; Time, 30 Minutes; Amount of Hanus Solution Varied]

Amount Hanus solution (cc)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Amount Hanus solution (cc)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(a) Raw Oil					(c) Burnt Linseed Oil No. "00"—Con.				
20	0.4737	0.3258	162.9	.....					
20	0.4737	0.3271	163.6	.....					
20	0.4737	0.3266	163.3	163.6	40	1.0816	0.2980	149.0	149.4
25	0.5928	0.3619	181.0	.....	50	1.3520	0.3054	152.7	.....
25	0.5928	0.3615	180.8	.....	50	1.3520	0.3044	152.2	152.4
25	0.5928	0.3609	180.5	180.8	60	1.6224	0.3052	152.6	152.6
30	0.7114	0.3747	187.4	.....	70	2.0280	0.3066	153.3	.....
30	0.7114	0.3754	187.7	187.6	70	2.0280	0.3060	153.0	153.1
35	0.8300	0.3822	191.1	.....	(d) Burnt Linseed Oil No. 3				
35	0.8300	0.3820	191.0	.....					
35	0.8300	0.3816	190.8	191.0	20	0.4622	0.1940	97.0	.....
40	0.9486	0.3831	191.6	.....	20	0.4622	0.1932	96.6	96.8
40	0.9486	0.3806	190.3	191.0	25	0.5778	0.2128	106.4	.....
50	1.1862	0.3832	191.6	191.6	25	0.5778	0.2152	107.6	.....
60	1.4235	0.3840	192.0	.....	25	0.5778	0.2152	107.6	107.2
60	1.4235	0.3824	191.2	191.6	30	0.6933	0.2284	114.2	.....
75	1.7793	0.3846	192.3	.....	30	0.6933	0.2282	114.1	114.1
75	1.7793	0.3828	191.4	191.8	40	0.9244	0.2444	122.2	.....
(b) Boiled Oil					40	0.9244	0.2438	121.9	.....
20	0.5522	0.3490	174.5	.....	40	0.9244	0.2432	121.6	121.9
20	0.5522	0.3472	173.9	174.2	50	1.1556	0.2488	124.4	.....
25	0.6902	0.3580	179.0	.....	50	1.1556	0.2488	124.4	124.4
25	0.6902	0.3574	178.7	.....	60	1.3866	0.2518	125.9	.....
25	0.6902	0.3560	178.0	178.6	60	1.3866	0.2506	125.3	125.6
30	0.8282	0.3606	180.3	.....	75	1.7334	0.2514	125.7	.....
30	0.8282	0.3606	180.3	.....	75	1.7334	0.2506	125.3	125.5
30	0.8282	0.3596	179.8	180.1	(e) Burnt Linseed Oil No. 5				
35	0.9662	0.3617	180.8	.....					
35	0.9662	0.3617	180.8	.....	20	0.4688	0.1966	98.3	.....
35	0.9662	0.3617	180.8	180 8	20	0.4688	0.1950	97.5	97.9
40	1.1044	0.3614	180.7	.....	25	0.5860	0.2148	107.4	.....
40	1.1044	0.3619	180.9	.....	25	0.5860	0.2140	107.0	107.2
40	1.1044	0.3634	181.7	181.1	35	0.8204	0.2440	122.0	.....
50	1.3759	0.3639	181.9	181.9	35	0.8204	0.2424	121.2	121.6
60	1.6510	0.3625	181.2	.....	50	1.1720	0.2602	130.1	.....
60	1.6510	0.3630	181.5	181.3	50	1.1720	0.2584	129.2	129.6
(c) Burnt Linseed Oil No. "00"					(f) Burnt Linseed Oil No. 5[9]				
					20	0.4688	0.1804	90.2	.....
20	0.5408	0.2640	132.0	.....	20	0.4688	0.1800	90.0	90.1
20	0.5408	0.2622	131.0	131.6	25	0.5860	0.1962	98.1	.....
25	0.6760	0.2820	141.0	.....	25	0.5860	0.1946	97.3	97.7
25	0.6760	0.2812	140.6	140.8	35	0.8204	0.2148	107.4	.....
30	0.8112	0.2992	149.6	.....	35	0.8204	0.2094	104.7	106.0
30	0.8112	0.2940	147.0	148.3	50	1.1720	0.2218	110.9	.....
40	1.0816	0.2996	149.8	.....	50	1.1720	0.2186	109.3	110.1

[9] Temperature 0° C.

TABLE 3

Linseed Oil

[Temperature 25°; 0.2-g Oil; 25-cc Hanus Solution; Time of Absorption Varied]

Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(a) Raw Oil					(d) Burnt Linseed Oil No. "00" Contd				
5	0.5972	0.3284	164.2	.....	15	0.5606	0.2495	124.8	.....
5	0.5972	0.3281	164.1	164.2	15	0.5606	0.2486	124.3	.....
15	0.5972	0.3497	174.9	.....	15	0.5606	0.2501	125.1	124.9
15	0.5972	0.3495	174.8	.....	30	0.5606	0.2584	129.2	.....
15	0.5972	0.3493	174.7	174.8	30	0.5606	0.2579	129.0	129.1
30	0.5972	0.3629	181.5	.....	30	0.5606	0.2607	130.4	.....
30	0.5972	0.3625	181.3	.....	45	0.5606	0.2593	129.7	.....
30	0.5972	0.3616	180.8	181.2	45	0.5606	0.2586	129.3	129.8
45	0.5972	0.3677	183.9	.....	60	0.5606	0.2635	131.8	.....
45	0.5972	0.3680	184.0	184.0	60	0.5606	0.2614	130.7	.....
60	0.5972	0.3737	186.9	.....	60	0.5606	0.2642	132.1	.....
60	0.5972	0.3736	186.8	.....	60	0.5606	0.2628	131.4	131.5
60	0.5972	0.3733	186.7	186.8	(e) Burnt Linseed Oil No. "1"				
(b) Boiled Oil					5	0.5746	0.2310	115.5	.....
5	0.6811	0.3380	169.0	.....	5	0.5746	0.2310	115.5	115.5
5	0.6811	0.3342	167.1	168.0	15	0.5746	0.2405	120.3	.....
15	0.6811	0.3518	175.9	.....	15	0.5746	0.2436	121.8	.....
15	0.6811	0.3510	175.5	.....	15	0.5746	0.2405	120.3	.....
15	0.6811	0.3508	175.4	175.6	15	0.5746	0.2440	122.0	.....
20	0.6811	0.3548	177.4	177.4	15	0.5746	0.2426	121.3	121.1
30	0.6811	0.3556	177.8	177.8	30	0.5746	0.2500	125.0	.....
45	0.6811	0.3600	180.0	.....	30	0.5746	0.2497	124.9	.....
45	0.6811	0.3602	180.1	180.0	30	0.5746	0.2493	124.7	.....
60	0.6811	0.3602	180.1	.....	30	0.5746	0.2496	124.8	124.9
60	0.6811	0.3592	179.6	179.9	45	0.5746	0.2540	127.0	.....
(c) Boiled Oil[10]					45	0.5746	0.2519	126.0	.....
5	0.6760	0.3282	164.1	.....	45	0.5746	0.2525	126.3	126.4
5	0.6760	0.3266	163.3	163.7	60	0.5746	0.2540	127.0	.....
10	0.6760	0.3422	171.1	.....	60	0.5746	0.2552	127.6	.....
10	0.6760	0.3402	170.1	170.6	60	0.5746	0.2554	127.7	.....
15	0.6760	0.3466	173.3	.....	60	0.5746	0.2559	128.0	127.6
15	0.6760	0.3462	173.1	173.2	(f) Burnt Linseed Oil No. "3"				
30	0.6760	0.3490	174.5	.....	5	0.6691	0.2252	112.6	.....
30	0.6760	0.3506	175.3	174.9	5	0.6691	0.2252	112.6	112.6
45	0.6760	0.3528	176.4	176.4	15	0.6691	0.2394	119.7	.....
60	0.6760	0.3528	176.4	.....	15	0.6691	0.2374	118.7	.....
60	0.6760	0.3518	175.9	176.2	15	0.6691	0.2402	120.1	.....
(d) Burnt Linseed Oil No. "00"									
5	0.5606	0.2405	120.3	.....					
5	0.5606	0.2406	120.3	120.3					
15	0.5606	0.2509	125.5	.....					

[10] Temperature 0°

TABLE 3—Continued

Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average	Time (min.)	Iodine added (grams)	Iodine absorbed (grams)	Iodine No.	Average
(f) Burnt Linseed Oil No. "3"—Contd					(g) Burnt Linseed Oil No. "5"—Contd				
15	0.6691	0.2367	118.4	119.2	5	0.6689	0.2120	106.0	.....
30	0.6691	0.2472	123.6	.....	5	0.6689	0.2136	106.8	106.5
30	0.6691	0.2483	124.2	.....	15	0.6689	0.2309	116.9	.....
30	0.6691	0.2480	124.0	123.9	15	0.6689	0.2271	115.0	.....
45	0.6691	0.2532	126.6	.....	15	0.6689	0.2271	115.0	.....
45	0.6691	0.2532	126.6	.....	15	0.6689	0.2271	115.0	115.5
45	0.6691	0.2525	126.3	126.5	30	0.6689	0.2390	119.5	.....
60	0.6691	0.2539	127.0	.....	30	0.6689	0.2390	119.5	119.5
60	0.6691	0.2539	127.0	.....	45	0.6689	0.2411	120.6	.....
60	0.6691	0.2542	127.1	127.0	45	0.6689	0.2411	120.6	.....
(g) Burnt Linseed Oil No. "5"					45	0.6689	0.2425	121.3	120.8
					60	0.6689	0.2432	121.6	.....
					60	0.6689	0.2432	121.6	121.6
5	0.6689	0.2145	107.3	.....					
5	0.6689	0.2118	105.9	.....					

TABLE 4

Petroleum Oils

[Temperature, 25°; Time, 30 Minutes; 25-cc Hanus Solution]

Oil (grams)	Iodine absorbed (grams)	Iodine No.	Oil (grams)	Iodine absorbed (grams)	Iodine No.
(a) Light Oil No. 1			(c) Engine Oil		
			0.0202	0.0167	77.9
0.2313	0.0683	29.5	0.0418	0.0307	69.4
0.5896	0.1454	24.7	0.0644	0.0448	65.7
0.7542	0.1756	23.3	0.1312	0.0735	52.9
0.9222	0.2006	21.8	0.1683	0.0870	48.8
1.0322	0.2105	20.4	0.1932	0.0953	46.6
1.5037	0.2621	17.4	1.009	0.2202	21.9
2.3203	0.3288	14.2	1.059	0.2235	21.1
(b) Light Oil No. 2			1.167	0.2371	20.3
			1.203	0.2423	20.1
0.2381	0.0807	33.9	1.305	0.2516	19.3
0.5144	0.1363	26.5	2.069	0.3058	14.8
0.6800	0.1678	24.6			
1.0288	0.2145	20.9			
1.6731	0.2819	16.9			
2.5151	0.3429	13.6			

[Temperature, 25°; Time, 3 Hours; 25-cc Hanus Solution]

(d) Engine Oil			(d) Engine Oil—Continued		
0.2608	0.1328	50.9	1.169	0.2873	24.6
0.4382	0.1766	40.3	1.839	0.3474	13.5
0.8298	0.2391	28.8			
1.139	0.2854	25.0			

V. DISCUSSION OF RESULTS

TABLE 1

Table 1, the results of which are plotted in Figs. 1 and 2, show the difference in behavior of the various linseed oils when the amount of iodine solution added is kept constant and the weight of oil is varied. Fig. 1 shows the change in iodine number with increasing amounts of oil. The curves in Fig. 2 have been calculated from the data given in Table 1 to represent the change in iodine number with a decrease in the excess of iodine present. It will be of interest to compare these curves with those in Fig. 3. The striking point in this connection is the range in weight of oil over which the iodine number is constant in the raw and boiled oils, as compared with that of the burnt oils.

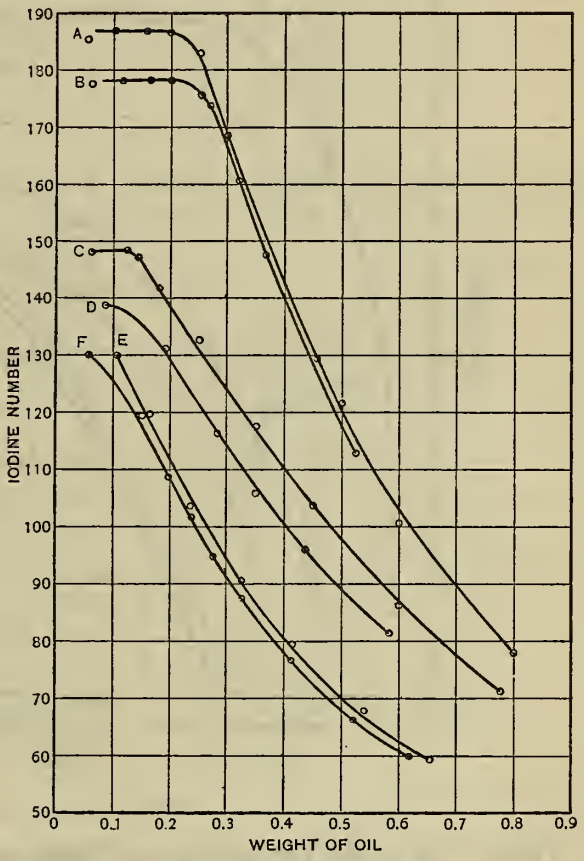

Fig. 1.—*Weight of oil varied*

It will be seen that, contrary to the general opinion, the oil with the highest iodine number does not require the largest excess of iodine to reach a maximum absorption value. It is not desirable to work with less than 0.1 gram of oil, because of the difficulty in obtaining constant values. Between 0.1 and 0.2 gram small varia-

tions in weight are negligible in raw and boiled oils, but are important in the burnt oils.

It is apparent that substitution plays an important part in the reaction, and we will refer to this point later on.

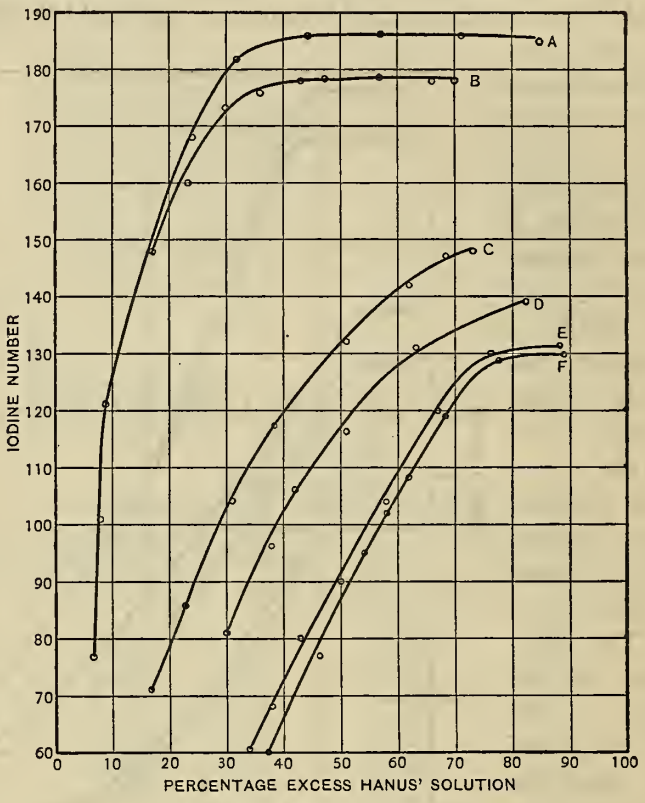

Fig. 2.—*Weight of oil varied*

TABLE 2

Table 2, in which the amount of Hanus solution is varied, is plotted in Fig. 3. Even more clearly than Fig. 2 does this show that burnt linseed oils do not readily reach a maximum.

The factor excess of iodine may be varied by changing the weight of oil or the amount of Hanus solution. In either case the effect upon the iodine number is about the same.

It is not sufficient, however, merely to specify the percentage excess of iodine, as the following figures, taken from Tables 1 and 2, will show:

Sample	0.1-gram oil 25-cc Hanus solution	0.2-gram oil 50-cc Hanus solution
Raw	186.4	191.6
Boiled	178.5	181.9
No. 00	139.5	152.4
No. 3	111.0	124.4
No. 5	109.0	129.6

These figures, together with the results shown in the preceding tables (1 and 2), demonstrate clearly that in these oils at least an iodine number should always be accompanied by full data as to the conditions under which it is determined, in order that it may be used for comparison.

When dealing with unknown oils it will probably be found satisfactory to determine the iodine value for several weights of oil, other conditions being held constant. For convenience we would recommend the use of 25 cc of Hanus solution and 30 minutes' absorption. When testing for the purity of a sample of oil a sample of known purity could be used as a standard, and by determining the iodine number on both samples under identical conditions adulteration or inferior quality should be readily detected.

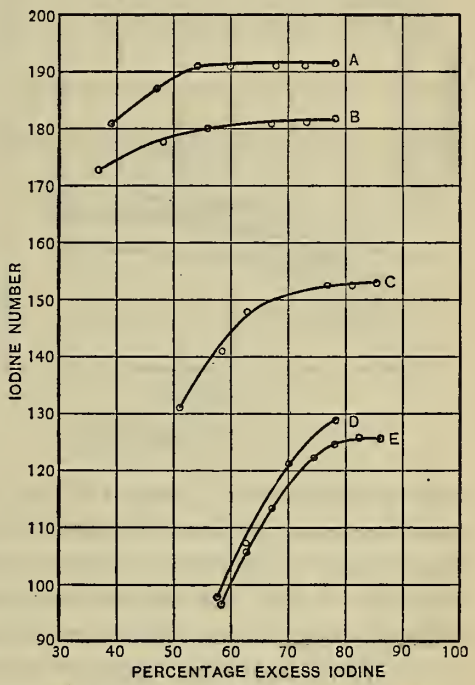

Fig. 3.—*Amount of Hanus solution varied*

The curve for Table 2 (*f*) will be found on Fig. 6, and will be referred to later. It is placed here so as to contrast it with the results given in Table 2 (*e*).

TABLE 3

The results of Table 3 (omitting (*c*)) are shown in Fig. 4. They show that after the first five minutes the absorption is slow, and the difference of a few minutes one way or the other after 15 minutes, will have little effect on the iodine value. Thirty minutes should prove a very satisfactory time and is now generally adopted.

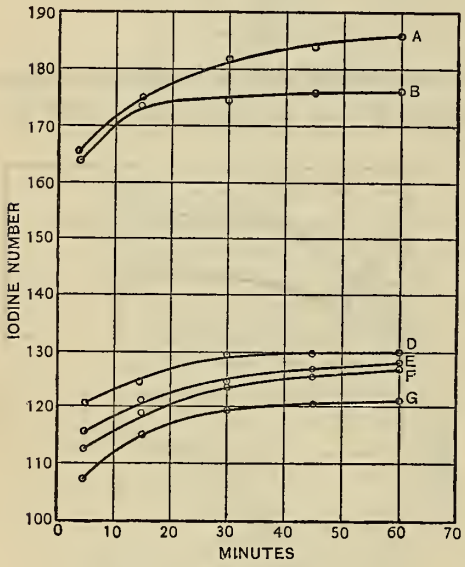

Fig. 4.—*Time of absorption varied*

Figs. 5, 6 contain two sets of curves showing the effect of temperature. Table 3 (*b*) and (*c*) show that, other conditions being equal, small differences in temperature at which an iodine value is obtained are negligible, so far as boiled oils are concerned, and presumably raw oils also, since their behavior is very much like that of the former. This is not, however, true of the burnt linseed oils, as inspection of the curves for Table 2 (*e*) and (*f*) will readily show. Using the largest practical excess of iodine, the difference between the results obtained at the two temperatures is too great to be considered negligible. Moreover, the fact that the curves are not even approximately parallel makes it difficult to allow for differences in temperature.

It will be seen that about 90 per cent of the absorption occurs in the first five minutes. If we assume that the addition of iodine is nearly instantaneous, and the substitution that part of the reaction which continues over a wide range of time, it is evident that any lessening of the time of absorption, which will at best eliminate only a small part of the total substitution, may give

low values which properly belong on the portion of the curve which is rapidly changing its slope.

A study of the effect of temperature on substitution is a more promising field than that of the time factor. Tables 2 (e) and 2 (f) as plotted in Fig. 6, show that at the lower temperature the effect of increasing the excess of iodine is less than at the higher one. The difference in the iodine values between 15 and 30 minutes is about 5 units (see Fig. 4), whereas the difference between 25° C and 0° C, at the maximum percentage excess of iodine employed, is 20 units. (See Fig. 6.)

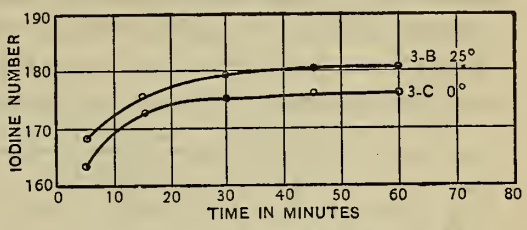

Fig. 5.—*Time and temperature varied*

TABLE 4

Fig. 7 shows clearly the futility of attempting to reach a constant value for mineral oils by increasing the excess of iodine. For the smaller quantities of oil used in the determination slight changes in the amount of oil taken cause large differences in the iodine number. Undoubtedly the lower values are more nearly correct than the higher ones, and therefore increasing the excess of iodine increases materially the error involved. To obtain concordant results the weight of oil and amount of iodine solution must be defined within very narrow limits. Our results indicate that not less then 1 gram of oil should be employed for the determination, with 25 cc of the iodine solution.

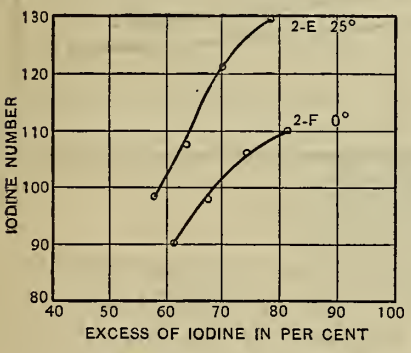

Fig. 6.—*Temperature and excess iodine varied*

It is interesting to contrast the behavior of linseed oils with that of mineral oils. The former tend to approach a constant value with a decreasing weight of oil, or increasing excess of iodine,

while, on the contrary, the latter tend to approach a constant value with increasing weight of oil.

VI. SUMMARY

The iodine values of raw, boiled, and burnt linseed oils were determined by the Hanus method, varying widely the amounts of oil and iodine used and the time of absorption.

It is shown that in order to obtain concordant results for iodine absorption a prescribed procedure must be followed exactly.

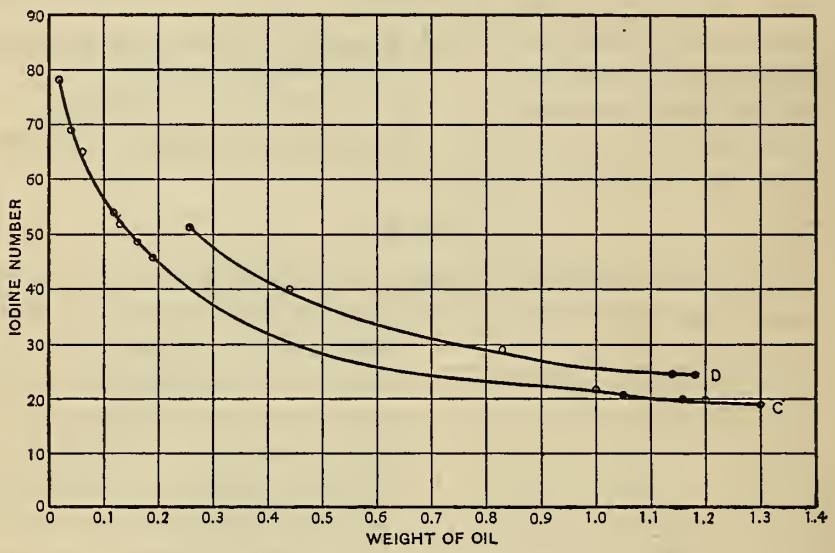

Fig. 7.—*Weight of engine oil varied*

To obtain comparable results a standard procedure should be adopted in which the limits are more exactly defined than is true at present. This is particularly necessary in the case of burnt linseed oils. With raw linseed oil a constant value is reached within comparatively wide limits of weight of oil and excess of iodine.

A study was made of the effect of temperature on the iodine absorption, from which it would appear that it may be feasible to improve the Hanus method by working at lower temperatures than those which have been used, and thus eliminate part of the substitution which occurs simultaneously with the addition.

The results obtained show that when used under exact conditions the Hanus method is to be recommended for simplicity of preparation of the solutions employed, ease of manipulation, and for concordance of results obtained.

Suggestions are made for the standardization of the method of determining the iodine number of mineral oils. The necessity for such action is shown by the results on several samples of lubricating oils.

We wish to express our appreciation of the courtesy of Messrs. Ault & Wiborg, of Cincinnati, Ohio, in furnishing us with the burnt linseed oils used in this work.

WASHINGTON, April 28, 1914.